Understanding Devitrification Pathways in Metallic Glasses

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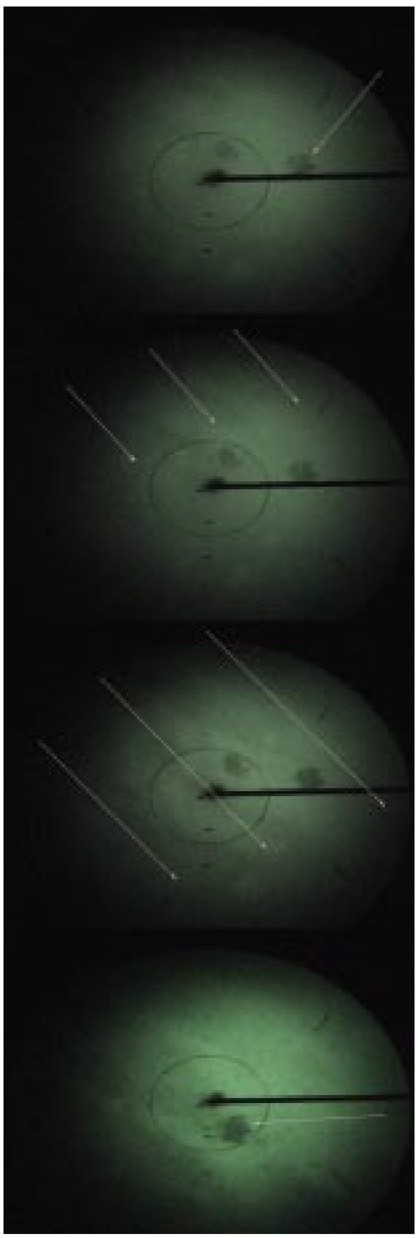
Abstract:

The project is directed toward obtaining a more comprehensive understanding of the underlying thermodynamics, nucleation and kinetics that dictate the decomposition pathways available in metallic glasses. Current primary interest is to determine and model the active nucleation and growth processes that control the development of the high density ($>10^{21}$ sites/m^3) of Al nanocrystals, quasicrystal formation and the related initial atomistic configuration of the metallic glass.

Recent Results:



While the effort in this area started only recently (October 1, 2001), it is based on past experience and knowledge of Al-based glass forming systems. In previous work by Perepezko and Foley various aspects of the devitrification of Al-based glasses were reported. However, several scientific questions still remain unanswered. One of the most elusive questions relates to the mechanism active to form a high density ($>10^{21}$ sites/m^3) of Al nanocrystals within an amorphous matrix. Currently, it is not understood or agreed upon why many of the Al-based alloys decompose to a microstructure consisting of a high density ($>10^{21}$ sites/m^3) of Al nanocrystals within an amorphous matrix. It has been reported by Gangopadhyay, Croat and Kelton that a melt-spun ribbon of Al-6at%Gd-2at%La-4at%Ni undergoes a spinodal decomposition that enables a high density of primary Al nanocrystals to form. In the same work it was postulated that similar spinodal decomposition also occurs in the Al-Y-Fe, Al-Y-Ni and other Al-Rare-earth-Transition metal (Al-RE-TM) systems. However, recent work by Kelton reports that no evidence of phase separation was observed in Al-7at%Y-5at%Fe melt-spun ribbon. Also of interest is directly observing the formation of a higher density of Al nanocrystals during continuous heating of melt-spun ribbon to just above the onset of the characteristic peak observed in many Al-based glass forming alloys. It was shown by Perepezko and Foley that an order-of-magnitude more nanocrystals form when the as-spun ribbon is taken to just above the onset of the characteristic peak and then quenched. It was postulated that diffusion conditions change dramatically enough to enable additional nucleation of Al nanocrystals; however, no direct evidence was ever obtained. In-situ TEM measurements may allow for observation of the location and magnitude of the nucleation events. An example of preliminary in-situ TEM results can be seen in the four selected frame images to the left. In the first frame the microstructure consists of a two-phase microstructure consisting of Al nanocrystals in an amorphous matrix. The Al nanocrystals formed during heating in the microscope, but their growth was not detected due the difficulty in maintaining focus in the sample during heating. However, the crystallization of the remaining amorphous structure was detected and the progression is shown in the second and third frame by the tips of the arrows. The fourth frame shows how the Al nanocrystal, shown in first frame has changed morphology due to the second decomposition reaction. These initial in-situ TEM results indicate that a similar microstructure is obtained from the in-situ TEM compared to previous standard TEM results. Additional research is needed to look at possible non-uniform temperature issues. Preliminary in-situ X-ray work indicates that it is very sensitive to small variations in structure and research is needed to obtain a minimum nanocrystal detection size. Ultrasonic results indicate that measurements can be conducted on melt-spun ribbon using a rod wave to obtain the ribbons absolute modulus assuming an accurate measure of the ribbon's density can be obtained. Further work is needed to determine if the formation and growth of Al nanocrystals can be measured ultrasonically similar to free volume changes.

Significance:

Currently there is scientific disagreement over the devitrification pathway many metallic glasses follow. Reports of homogeneous nucleation, heterogeneous nucleation and spinodal decomposition (i.e., phase separation) for the same alloy system and composition exist. Moreover, while there are hypotheses presented in the literature for the relatively high density of Al nanocrystals, there is no generally accepted theory or model. The current work will provide insight into the issue by elucidating the transformation mechanism associated with specific devitrification pathways.

Future Work:

Initial work will concentrate on determining the transformation processes that control the development of the unique devitrification nanostructure in Al-Y-Fe, Al-Y-Ni and Al-La-Gd-Ni. Our effort will use in-situ TEM and in-situ X-ray diffraction to characterize the devitrification pathway and critically test the different proposed devitrification mechanisms. The X-ray studies will be performed in collaboration with M. J. Kramer. It is believed that the capabilities of the facilities at Argonne National Laboratory's Advanced Photon Source may be able to detect the presence of quenched-in nanocrystals hypothesized to exist in Al-Y-Fe alloys. In addition, the in-situ X-ray diffraction during heating will provide crystalline structure information that will complement the thermal and microstructural analyses. The combination of careful thermal analysis, in-situ TEM and structural analyses using synchrotron X-rays will provide valuable data for interpreting any correlations between initial short-range atomic order and the devitrification behavior in amorphous systems.

In addition, it is anticipated that the in-situ TEM work will allow for unambiguous determination of the pathway to the formation of dendrite-like nanocrystals after extended annealing at temperatures approaching, but below Tg. It has been speculated that the dendritic features in nanocrystals are develop either by a growth or a nucleation phenomenon. In-situ observation should help identify the formation route and may help determine why the dendrite-like nanocrystals exist. Moreover, the in-situ observation should have relevance to the Solidification Science focus area since it would be direct observation of the growth of a metallic dendrite in a highly undercooled liquid. Along with the in-situ work, ultrasonic measurements will be explored as a way to monitor atomic rearrangement, such as glass relaxation and spinodal decomposition. These are not easily observed with other characterization techniques. Moreover, limited quantitative and qualitative data exist about the structural relaxation in Al-based metallic glasses before devitrification. The known high sensitivity of ultrasonic wave velocity to free volume changes should provide an increased understanding about possible structural changes that occur below the glass transition.

Interactions:

We are working closely with M.J. Kramer to examine devitrification with in-situ X-ray diffraction experiments. The in-situ TEM work is a partnership with the efforts of F.C. Laabs. It is also expected that our efforts will require extensive collaboration with D.J. Sordelet, especially when examining metallic glass systems that form a quasicrystalline phase during devitrification.